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Signed this 18th day of January 2002



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Director

For and on behalf of RWS Group plc

TRANSLATION FROM JAPANESE

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(54) Title of the Invention: **Aqueous Pigment Dispersion**

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## **SPECIFICATION**

### **1. Title of the Invention**

Aqueous Pigment Dispersion

### **2. Claims**

An aqueous pigment dispersion, comprising a pigment, a dispersant, and an aqueous medium, wherein said aqueous pigment dispersion is characterized in that the dispersant is an aqueous copolymerization product obtained by copolymerizing:

(A) 5–95 weight parts of a fatty acid-modified (meth)acrylic monomer;

(B) 0.5–93 weight parts of a macromonomer having on one end thereof at least one type of vinyl-polymerizable functional group selected from acryloyloxy, methacryloyloxy, allyloxy, and aromatic vinyl;

(C) 2–90 weight parts of an  $\alpha,\beta$ -ethylenic, unsaturated, nitrogen-containing monomer;

(D) 0–20 weight parts of an  $\alpha,\beta$ -ethylenic unsaturated carboxylic acid; and

(E) 0–91 weight parts of an  $\alpha,\beta$ -ethylenic unsaturated monomer other than the ones described in (A) to (D) above.

### **3. Detailed Description of the Invention**

The present invention relates to an aqueous pigment dispersion that has excellent storage stability and can be readily manufactured using a novel dispersant.

It is common knowledge that flushing, floating, deglossing, loss of colour on a coating surface, and other undesirable changes are induced by the aggregation and precipitation of pigments during storage or by the impaired dispersibility of pigments in production processes aimed at obtaining water-based paints such as pigment-containing emulsion paints and water-soluble resin paints. For this reason, an aqueous pigment dispersion is first prepared by dispersing a pigment with a

dispersant, and this dispersion is then admixed with, or dispersed in, the water-based paint being coloured.

Low-molecular-weight compounds such as surfactants have come to be used as dispersants for such conventional aqueous pigment dispersions, but these dispersants always have detrimental secondary effects on the performance or properties of paint films. Such effects are currently suppressed by the use of dispersants in the form of oligomers or polymers with intermediate molecular weights.

Using such oligomer or polymer dispersants is disadvantageous, however, in the sense that their consumption is greater than that of low-molecular-weight surfactants and that the resulting aqueous pigment dispersion can be used only in a limited number of applications. The scope of these applications is determined by the types of binder used for water-based paints. This restriction inhibits progress in paint production and creates an urgent need for developing an aqueous pigment dispersion that can be used with a variety of water-based paints.

The present applicant has previously proposed a copolymer (JP (Kokai) 59-227940) obtained by copolymerizing a fatty acid-modified (meth)acrylic monomer, a nitrogen-containing monomer, and an ethylenic unsaturated carboxylic acid and used as a dispersant component that can facilitate pigment dispersion with small amounts, that is compatible with numerous aqueous resins, and that is itself a polymer with no adverse effect on the performance of a film composed of a water-based paint.

An aqueous pigment dispersion obtained using such a dispersant, while providing excellent pigment dispersibility during production, is still disadvantageous in that pigment particles coalesce and form a partially or completely solid cake when the dispersion is stored for a long time, making it impossible to return the dispersion to its pre-storage condition even after being redispersed by a stirrer or the like and creating creeping, deglossing, and other defects in the paint film.

The inventors perfected the present invention upon discovering that the storage stability of an aqueous pigment dispersion can be improved without impairing the excellent dispersibility, compatibility, paint film performance, and other properties of a copolymer used as a dispersant for an aqueous pigment dispersion when this dispersant is a copolymer obtained by combining the aforementioned monomer components with a long-chain macromonomer.

Thus, the present invention offers an aqueous pigment dispersion comprising a pigment, a dispersant, and an aqueous medium, wherein this aqueous pigment dispersion is characterized in that the dispersant is an aqueous copolymerization product obtained by copolymerizing the following components:

(A) 5–95 weight parts of a fatty acid-modified (meth)acrylic monomer;

(B) 0.5–93 weight parts of a macromonomer having on one end thereof at least one type of vinyl-polymerizable functional group selected from acryloyloxy, methacryloyloxy, allyloxy, and aromatic vinyl (this monomer will be referred to hereinbelow as a "macromonomer");

(C) 2–90 weight parts of an  $\alpha,\beta$ -ethylenic, unsaturated, nitrogen-containing monomer;

(D) 0–20 weight parts of an  $\alpha,\beta$ -ethylenic unsaturated carboxylic acid; and

(E) 0–91 weight parts of an  $\alpha,\beta$ -ethylenic unsaturated monomer other than the ones described in (A) to (D) above.

According to the present invention, the copolymer is structured such that the fatty acids derived from the fatty acid-modified (meth)acrylic monomer, and the long-chain components derived from the macromonomer are separate from the main chain with the hydrophilic nitrogen-containing monomer and ethylenic unsaturated carboxylic acid, so when this copolymer is used to disperse a pigment in water, the functional groups of the copolymer are adsorbed or deposited on the pigment particles, and some of the side chains separated from the main chain of the copolymer (particularly the long-chain components derived from the macromonomer) become

entangled with other long-chain components of the copolymer, thereby enveloping the pigment particles, forming a strongly hydrophobic barrier layer, and yielding a stable aqueous pigment dispersion. The pigment in the aqueous pigment dispersion is thus kept hydrophobic and is surrounded by a barrier layer containing unhydrolyzable components, making it possible to prevent the entry of water, alkali, and other substances and providing excellent storability without any precipitation or aggregation because the barrier layer is made up of components that possess increased steric hindrance and prevent pigment particles from moving closer to each other. In addition, the long-chain components of the copolymer can be introduced easily and securely by the use of the macromonomer component employed by the present invention. Another feature is that a coloured paint film with an excellent performance in terms of water resistance and the like can be obtained because the dispersant has low acidity (that is, contains only a small number of carboxyl groups).

The dispersant used for the aqueous pigment dispersion of the present invention will now be described in further detail.

#### (A) Fatty Acid-modified (Meth)acrylic Monomer

The fatty acid-modified (meth)acrylic monomer used for the dispersant of the present invention may, for example, be one of the monomers disclosed in JP (Kokai) 60-81252. Examples include products obtained by reacting drying fatty acids, semidrying fatty acids, non-drying oil fatty acids, and other fatty acids with (meth)acrylic monomers whose functional groups can react with the carboxylic groups of the fatty acids.

Examples of suitable fatty acids include safflower oil fatty acids, linseed oil fatty acids, soybean oil fatty acids, sesame oil fatty acids, poppy oil fatty acids, eno oil fatty acids, hempseed oil fatty acids, grape seed oil fatty acids, corn oil fatty acids, tall oil fatty acids, sunflower oil fatty acids, cottonseed oil fatty acids, walnut oil fatty acids, rubber plant seed oil fatty acids, tung oil fatty acids, oiticica oil fatty acids, dehydrated castor oil fatty acids, Hy-diene fatty acids, and other drying and semidrying fatty acids; and coconut oil fatty acids, olive oil fatty acids, castor oil fatty acids, hydrogenated castor oil fatty acids, palm oil fatty acids, and other non-drying

fatty acids. These fatty acids may be used singly or as mixtures of two or more components.

The consumption of the aforementioned fatty acids varies widely with the drying properties or paint film properties required of the aqueous pigment dispersion provided by the present invention, and is commonly 5–65 wt%, and preferably 10–60 wt%, in relation to the weight of the resulting polymer.

Of the aforementioned fatty acids, drying or semidrying fatty acids with an iodine value of about 100 or greater are preferred from the standpoint of the present invention because such acids endow the resulting dispersant with crosslinking and drying properties at normal temperature.

The (meth)acrylic monomer introduced into such fatty acids may be an acrylic acid or methacrylic acid ester whose functional groups (such as epoxy or hydroxy groups) can react with the carboxyl groups of the fatty acids in the ester residue moiety. Specific examples include glycidyl (meth)acrylate, 2-hydroxyethyl (meth)acrylate, and 2-hydroxypropyl (meth)acrylate.

#### (B) Macromonomer

In the macromonomer used in the present invention, the main molecular chain is a vinyl-based polymer, and one end of the main chain has a radical-polymerizable unsaturated group such as acryloyloxy, methacryloyloxy, allyloxy, or aromatic vinyl.

The components of the aforementioned molecular chain may be obtained by homopolymerizing or copolymerizing one, two, or more of the monomers described below.

(1) Acrylic acid or methacrylic acid esters: Methyl acrylate, ethyl acrylate, propyl acrylate, isopropyl acrylate, butyl acrylate, hexyl acrylate, octyl acrylate, lauryl acrylate, methyl methacrylate, ethyl methacrylate, propyl methacrylate, isopropyl methacrylate, butyl methacrylate, hexyl methacrylate, octyl methacrylate, lauryl methacrylate, and other  $C_1$ – $C_{18}$  alkyl esters of acrylic acid or methacrylic acid; allyl acrylate, furyl methacrylate, and other  $C_2$ – $C_5$  alkenyl esters of acrylic acid and

methacrylic acid; hydroxyethyl acrylate, hydroxyethyl methacrylate, hydroxypropyl acrylate, hydroxypropyl methacrylate, and other  $C_2-C_6$  hydroxyalkyl esters of acrylic acid and methacrylic acid; and allyloxyethyl acrylate, allyloxymethacrylate, and other  $C_3-C_{18}$  alkenyloxy alkyl esters of acrylic acid and methacrylic acid.

(2) Vinyl aromatic compounds: Styrene,  $\alpha$ -methylstyrene, vinyltoluene, and *p*-chlorostyrene.

(3) Polyolefin-based compounds: Butadiene, isoprene, and chloroprene.

(4) Other: Acrylonitrile, methacrylonitrile, methyl isopropenyl ketone, vinyl acetate, VeoVa (from Shell Chemicals), vinyl propionate, vinyl pivalate, and the like.

Of the aforementioned monomers, compounds such as acrylic acid esters, methacrylic acid, and vinyl aromatic compounds are preferred from the standpoint of the rate of polymerization, copolymerization properties, and the like.

The macromonomer used in the present invention can be obtained in accordance with a conventional method by employing a prepolymer provided with a carboxyl group at one of its ends and obtained by polymerizing the aforementioned monomers in the presence of a chain transfer agent having carboxyl groups (such as thioglycolic acid) and a polymerization initiator (such as azobisisobutyronitrile or benzoyl peroxide), or by employing a prepolymer provided with a carboxyl group at one of its ends and obtained by polymerizing the aforementioned monomers in the presence of an azo-based polymerization initiator having carboxyl groups (such as azobiscyanovaleric acid) and a tertiary amine. The prepolymer is then reacted with a vinyl-based monomer whose functional groups can react with the carboxyl groups of the prepolymer. Typical examples of suitable vinyl-based monomers include glycidyl acrylate, glycidyl methacrylate, 2-hydroxyethyl acrylate, 2-hydroxyethyl methacrylate, 2-hydroxypropyl acrylate, 2-hydroxypropyl methacrylate, and other monomers having acryloyloxy or methacryloyloxy groups; allyl alcohol, allyl glycidyl ether, and other monomers having allyloxy groups; and *p*-isopropenyl phenylglycidyl ether, *p*-vinyl phenylglycidyl ether, and other monomers having aromatic vinyl groups.



The macromonomer used in the present invention should have a number-average molecular weight of 600–15,000, and preferably 1,000–10,000. A molecular weight less than 600 has an adverse effect on the storage stability of the aqueous pigment dispersion, whereas a molecular weight in excess of 15,000 disrupts the balance between the molecular weights of the main and side chains and has an adverse effect on the dispersibility of the pigment and the storage stability of the aqueous pigment dispersion.

Examples of suitable macromonomers include Aron Macromonomer MM-5AS (registered trade name of a polystyrene acrylonitrile product manufactured by Toagosei), Aron Macromonomer MM-5M (polymethyl methacrylate product from the same company), and Aron Macromonomer MM-5B (polybutyl acrylate product from the same company).

(C)  $\alpha,\beta$ -Ethylenic, Unsaturated, Nitrogen-containing Monomer

The  $\alpha,\beta$ -ethylenic, unsaturated, nitrogen-containing monomer (C) used for the dispersant of the present invention may be a monomer containing one or more (usually up to four) basic nitrogen atoms and one ethylenic unsaturated bond per molecule. Typical examples include unsaturated monomers having nitrogen-containing heterocycles, and nitrogen-containing derivatives of (meth)acrylic acid.

[1] The unsaturated monomer having nitrogen-containing heterocycles may be a monomer in which monocyclic or polycyclic heterocycles containing one to three (preferably one or two) cyclic nitrogen atoms are attached to a vinyl group. In particular, the following monomers can be cited.

(I) Vinyl Pyrrolidones

1-Vinyl-2-pyrrolidone, 1-vinyl-3-pyrrolidone, and the like.

(II) Vinyl Pyridines

2-Vinyl pyridine, 4-vinyl pyridine, 5-methyl-2-vinyl pyridine, 5-ethyl-2-vinyl pyridine, and the like.

(III) Vinyl Imidazoles

1-Vinylimidazole, 1-vinyl-2-methylimidazole, and the like.

(IV) Vinyl Carbazoles

*N*-vinyl carbazole and the like.

(V) Vinyl Quinones

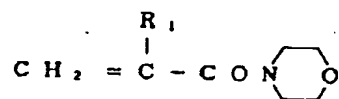
2-Vinyl quinone and the like.

(VI) Vinyl Piperidines

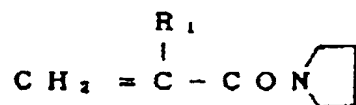
3-Vinyl piperidine, *N*-methyl-3-vinyl piperidine, and the like.

(VII) Other

*N*-(meth)acryloyl morpholines expressed, for example, by the formulas



(where  $\text{R}_1$  is a hydrogen atom or a methyl group), *N*-(meth)acryloyl pyrrolidines expressed by the formula

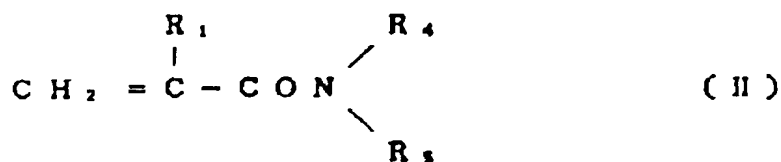
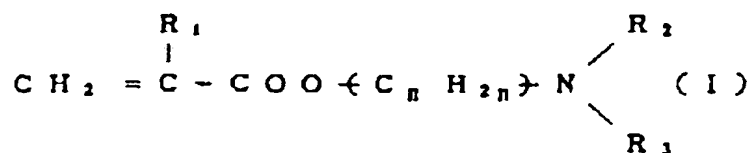


(where  $\text{R}_1$  is the same as above), and the like

Vinyl pyrrolidones, vinyl imidazoles, and vinyl carbazoles are preferred as such vinyl monomers having nitrogen-containing heterocycles, and monomers with tertiary cyclic nitrogen atoms are particularly preferred.

[2] The nitrogen-containing derivatives of (meth)acrylic acid include (meth)acrylic acid amides and compounds whose amino groups are unsubstituted or substituted by the ester moieties of (meth)acrylic acid esters. Particularly suitable are

the aminoalkyl (meth)acrylates and (meth)acrylamides expressed by formulas (I) and (II) below.



(where  $\text{R}_1$  is the same as above;  $\text{R}_2$  and  $\text{R}_3$  are each independently a hydrogen atom or a lower alkyl group;  $\text{R}_4$  is a hydrogen atom or a lower alkyl group;  $\text{R}_5$  is a hydrogen atom, a lower alkyl group, a di(lower alkyl)amino lower alkyl group, a hydroxy lower alkyl group, or a lower alkoxy lower alkyl group; and  $n$  is an integer from 2 to 8).

The term "lower" refers to a group with a carbon number of 6 or less, and preferably 4 or less.

Specific examples of such nitrogen-containing (meth)acrylic monomers include Formula (I) aminoalkyl (meth)acrylates such as *N,N*-dimethylaminoethyl (meth)acrylate, *N,N*-diethylaminoethyl (meth)acrylate, *N-t*-butylaminoethyl (meth)acrylate, *N,N*-dimethylaminopropyl (meth)acrylate, *N,N*-dimethylaminobutyl (meth)acrylate, *N*-propylaminoethyl (meth)acrylate, and *N*-butylaminoethyl (meth)acrylate; and Formula (II) (meth)acrylamides such as (meth)acrylamide, *N*-methyl (meth)acrylamide, *N*-ethyl (meth)acrylamide, *N*-butyl (meth)acrylamide, *N,N*-dimethyl (meth)acrylamide, *N,N*-diethyl (meth)acrylamide, *N,N*-dipropyl (meth)acrylamide, *N*-methylol (meth)acrylamide, *N*-ethoxymethyl (meth)acrylamide, *N*-butoxymethyl (meth)acrylamide, and *N,N*-dimethylaminopropyl acrylamide. Compounds with tertiary nitrogen atoms are preferred as such nitrogen-containing (meth)acrylic monomers, and compounds with secondary nitrogen atoms are less preferred.

The aforementioned  $\alpha,\beta$ -ethylenic, unsaturated, nitrogen-containing monomers can be used singly or as combinations of two or more monomers.

(D) Ethylenic Unsaturated Carboxylic Acid

The ethylenic unsaturated carboxylic acid (D) used for the dispersant of the present invention may be a polycarboxylic acid or an unsaturated aliphatic monomer of the type in which addition-polymerizable double bonds exist between the carbon atoms attached to carboxyl groups, and the carbon atoms adjacent thereto, with compounds having 3–8 carbon atoms (particularly 3–5 carbon atoms) and one or two carboxyl groups being particularly preferred. Typical examples include compounds expressed by General Formula (III)



(where  $R_6$  is a hydrogen atom or a lower alkyl group,  $R_7$  is a hydrogen atom, a lower alkyl group, or a carboxyl group, and  $R_8$  is a hydrogen atom, a lower alkyl group, or a carboxy lower alkyl group). In Formula (III) above, the lower alkyl group is a group with four or more carbon atoms, and preferably a methyl group.

Examples of such  $\alpha,\beta$ -ethylenic, unsaturated carboxylic acids include acrylic acid, methacrylic acid, crotonic acid, itaconic acid, maleic acid, maleic anhydride, and fumaric acid. These may be used individually or as combinations of two or more acids.

(E) Other  $\alpha,\beta$ -Ethylenic Unsaturated Monomer

The  $\alpha,\beta$ -ethylenic unsaturated monomer (E) other than those described in (A) to (D) above is not subject to any particular limitations and can be selected from a wide variety of monomers in accordance with the desired performance of the inventive dispersant. Any of the compounds described in the Macromonomer section above can be used as such an unsaturated monomer. Examples include acrylic acid or

methacrylic acid esters, alkenyl esters, hydroxyalkyl esters, alkenyloxy esters, vinyl aromatic compounds, polyolefin-based compounds, acrylonitrile, methacrylonitrile, methyl isopropenyl ketone, vinyl acetate, VeoVa monomer, vinyl propionate, and vinyl pivalate. Of these, acrylic acid or methacrylic acid esters and vinyl aromatic compounds are particularly preferred.

These unsaturated monomers can be appropriately selected in accordance with the desired physical properties and may be used either singly or as combinations of two or more monomers.

The above-described fatty acid-modified (meth)acrylic monomer (A), macromonomer (B),  $\alpha,\beta$ -ethylenic, unsaturated, nitrogen-containing monomer (C),  $\alpha,\beta$ -ethylenic unsaturated monomer (D), and unsaturated monomer (E) are polymerized with each other in accordance with the present invention. The components may be polymerized by a known method employed in the production of acrylic copolymers, such as solution polymerization, emulsion polymerization, or suspension polymerization.

The mixing ratios of the five polymerization components can be varied depending on the desired performance of the dispersant. The following mixing ratios are considered appropriate.

For the fatty acid-modified (meth)acrylic monomer (A), the range is 5–95 weight parts. A range of 10–85 weight parts is preferred from the standpoint of paint film drying and performance.

For the macromonomer (B), the range is 0.5–93 weight parts. A range of 1–60 weight parts is preferred from the standpoint of storage stability and pigment dispersion.

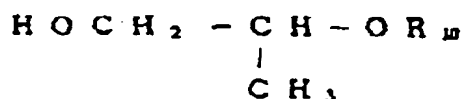
For the  $\alpha,\beta$ -ethylenic, unsaturated, nitrogen-containing monomer, the range is 2–90 weight parts. A range of 3–90 weight parts is preferred from the standpoint of pigment dispersibility.

For the  $\alpha,\beta$ -ethylenic unsaturated monomer (D), the range is 0–20 weight parts. A range of 2–18 weight parts is preferred from the standpoint of water solubility and paint film performance.

For an unsaturated monomer (E) other than (A) to (D) above, the range is 0–91 weight parts. A range of 5–83 weight parts is preferred from the standpoint of paint film performance.

The copolymerization reaction should preferably be carried out in accordance with a solution polymerization technique by allowing the aforementioned four components to react in the presence of a polymerization catalyst in an appropriate inert solvent for about 1 to 20 hours (preferably about 6 to 10 hours) at a reaction temperature that is commonly about 0–180°C, and preferably about 40–170°C.

The solvent must resist gelation during the copolymerization reaction, be able to dissolve the resulting copolymer, and be miscible with water. In particular, it is better to use a solvent that can yield an aqueous pigment dispersion without being removed. Examples of such solvents include ethyl glycol, butyl cellosolve, ethyl cellosolve, and other cellosolve-based solvents expressed by the formula  $\text{HO}-\text{CH}_2\text{CH}_2-\text{OR}_9$  (where  $\text{R}_9$  is a hydrogen atom or an alkyl group with one to eight carbon atoms); propylene glycol monomethyl ether and other propylene glycol solvents expressed by the formula



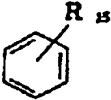
(where  $\text{R}_{10}$  is the same as above); diethylene glycol, methyl carbitol, butyl carbitol, and other carbitol-based solvents expressed by the formula

$\text{HO}-\text{CH}_2\text{CH}_2-\text{OCH}_2\text{CH}_2-\text{OR}_{10}$  (where  $\text{R}_{10}$  is the same as above); ethylene glycol dimethyl ether and other glyme-based solvents expressed by the formula

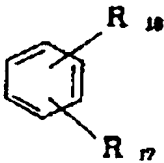
$\text{R}_{11}\text{O}-\text{CH}_2\text{CH}_2-\text{OR}_{12}$  (where  $\text{R}_{11}$  and  $\text{R}_{12}$  are each an alkyl group with one to three carbon atoms); diethylene glycol dimethyl ether and other diglyme-based solvents expressed by the formula  $\text{R}_{11}\text{O}-\text{CH}_2\text{CH}_2\text{OCH}_2-\text{CH}_2\text{OR}_{12}$  (where  $\text{R}_{11}$  and  $\text{R}_{12}$  are the same as above); ethylene glycol monoacetate, methyl cellosolve acetate, and other

cellosolve acetate solvents expressed by the formula  $R_{13}O-CH_2CH_2OCO-CH_3$  (where  $R_{13}$  is a hydrogen atom,  $CH_3$ , or  $C_2H_5$ ); and ethanol, propanol, and other alcohol-based solvents expressed by the formula  $R_{14}OH$  (where  $R_{14}$  is an alkyl group with one to four carbon atoms); as well as diacetone alcohol, dioxane, tetrahydrofuran, acetone, dimethylformamide, and 3-methoxy-3-methyl-butanol.

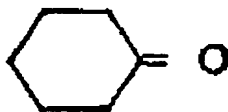
Inert solvents immiscible with water can also be used. Such water-immiscible solvents should preferably have a boiling point of  $250^\circ C$  or less to allow these solvents to be readily removed by distillation at normal or reduced pressure following the polymerization reaction. Examples of such solvents include toluene, xylene, and

other aromatic hydrocarbons expressed by the formula 

(where  $R_{15}$  is a hydrogen atom or an alkyl group with one to four carbon atoms) or the

formula 

(where  $R_{16}$  and  $R_{17}$  are each an alkyl group with one to four carbon atoms); acetic acid, ethyl formate, butyl acetate, cyclohexyl acetate, and other acids or esters expressed by the formula  $R_{18}-COO-R_{19}$  (where  $R_{18}$  is an alkyl group with one to six carbon atoms, and  $R_{19}$  is a hydrogen atom or an alkyl or cyclohexyl group with one to six carbon atoms); methyl ethyl ketone, cyclohexanone, and other ketones expressed by the formula  $R_{20}R_{21}C=O$  (where  $R_{20}$  and  $R_{21}$  are each an alkyl group with one to eight carbon atoms) or the formula



ethyl ether, hexyl ether, and other ethers expressed by the formula  $R_{20}-O-R_{21}$  (where  $R_{20}$  and  $R_{21}$  are the same as above); and hexanol and other alcohols expressed by the formula  $R_{22}OH$  (where  $R_{22}$  is an alkyl group with 5 to 11 carbon atoms).

These solvents can be used in an amount of 15–90 wt% in relation to the combined weight of the aforementioned four polymerization components.

Examples of suitable polymerization catalysts include azo-based compounds, peroxide-based compounds, sulphides, sulphines, sulphinic acids, diazo compounds, nitroso compounds, redox systems, ionising radiation, and other radical initiators commonly used to achieve radical polymerization.

Although the polymer for the dispersant of the inventive aqueous pigment dispersion is usually prepared by copolymerizing monomers (A) to (E) in the above-described manner, it is also possible to adopt an approach whereby a copolymer containing carboxyl groups is obtained by copolymerizing monomers (B) to (E) (excluding monomer (A)), and this copolymer is then reacted with soybean oil fatty acid glycidyl ester, safflower oil fatty acid glycidyl ester, linseed oil fatty acid glycidyl ester, or another fatty acid glycidyl ester.

The present invention also allows a substantially satisfactory aqueous pigment dispersion to be obtained from a copolymer that has a different molecular weight. An excessively low molecular weight, however, creates the danger that the paint film properties of the coloured water-based paint will be adversely affected. An excessively high molecular weight will result in higher viscosity. Selecting a lower viscosity reduces copolymer concentration and has an adverse effect on pigment dispersibility. For this reason, the copolymerization reaction should preferably be performed until the number-average molecular weight of the resulting copolymer falls within a range of about 1,000–150,000, and preferably about 1,500–100,000.

The copolymer resin thus obtained is solubilised in water either directly or following solvent removal. The copolymer can be solubilised in water by an ordinary method, such as neutralizing the carboxyl groups present in the copolymer resin with a conventional neutralizing agent. Examples of suitable neutralizing agents include ammonia, amines, alkali metal hydroxides, and alkali metal carbonates or bicarbonates. Examples of suitable amines include primary, secondary, and tertiary alkylamines; primary, secondary, and tertiary alkanolamines; and cycloalkylamines. Examples of suitable alkali metal hydroxides include potassium hydroxide and



sodium hydroxide. Examples of suitable alkali metal carbonates and bicarbonates include potassium carbonate, sodium carbonate, and sodium bicarbonate.

The neutralization process can be readily performed by an ordinary method by adding one of the above-described neutralizing agents or an aqueous solution thereof to the copolymer or a solution thereof. The neutralizing agent is used in an amount that is commonly 0.1–2.0 equivalents, and preferably 0.3–1.0 equivalents, in relation to the carboxyl groups in the resin.

The water-solubilised polymer thus obtained can be used as a dispersant for aqueous pigment dispersions composed of pigments, dispersants, and aqueous media.

The dispersant composed of a water-solubilised polymer should be used in an amount of about 1–500 weight parts, and preferably about 1–300 weight parts, per 100 weight parts of pigment. Exceeding this range tends to create an imbalance between the viscosity and tinting strength of the aqueous pigment dispersion, whereas moving past the lower limit tends to have an adverse effect on the dispersion stability of the pigment.

Although the aqueous medium used for the aqueous pigment dispersion of the present invention is essentially water, hydrophilic organic solvents can also be used as needed in cases in which, for example, the dispersant has weak hydrophilic properties and fails to produce an adequate pigment dispersion. Compounds used in the production of the above-described polymers can be used, either singly or as mixtures, for such hydrophilic organic solvents.

The pigment for the aqueous pigment dispersion of the present invention may be any inorganic or organic pigment commonly used for such pigment dispersions. Examples of inorganic pigments include (1) oxides (zinc oxide, titanium dioxide, Indian red, chromium oxide, cobalt blue, black iron oxide, and the like), (2) hydroxides (alumina white, yellow iron oxide, and the like), (3) sulphides and selenides (zinc sulphide, vermilion, cadmium yellow, cadmium red, and the like), (4) ferrocyanides (Prussian blue and the like), (5) chromates (chrome yellow, zinc chromate, molybdenum red, and the like), (6) sulphates (precipitating barium sulphate

and the like), (7) carbonates (precipitating calcium carbonate and the like), (8) silicates (hydrated silicates, clay, ultramarine, and the like), (9) phosphates (manganese violet and the like), (10) carbon materials (carbon black and the like), and (11) metal powders (aluminum powder, bronze powder, zinc powder, and the like). Examples of organic pigments include (1) nitroso pigments (Naphthol Green B and the like), (2) nitro pigments (Naphthol Yellow S and the like), (3) azo pigments (Lithol Red, Lake Red C, Fast Yellow, Naphthol Red, Red, and the like), (4) dye lake pigments (Alkali Blue Lake, Rhodamine Lake, and the like), (5) phthalocyanine pigments (Phthalocyanine Blue, Fast Sky Blue, and the like), and (6) condensed polycyclic pigments (Perylene Red, Quinacridone Red, Dioxazine Violet, Isoindolinone Yellow, and the like).

The amount in which the pigment is contained in the aqueous pigment dispersion of the present invention is not subject to any particular limitations and is generally about 2–90 wt%, based on the weight of the dispersion.

The aqueous pigment dispersion of the present invention can be prepared by mixing together the aforementioned components in an appropriate dispersing apparatus, examples of which include the following devices commonly used in the paint industry: ball mills, roll mills, homomixers, sand grinders, shakers, and attritors.

Conventional surfactants or protective colloids may further be added as needed to the aqueous pigment dispersion of the present invention.

The aqueous pigment dispersion of the present invention is readily miscible with conventional emulsions, water-dispersible resins, and water-soluble resins such as alkyd resins, acrylic resins, epoxy resins, urethane resins, maleinised polybutadiene resins, and other resins commonly used for water-based paints and water-based inks. These resins do not impose any limitations on the process, allowing a water-based paint composed of any resin to be coloured.

In a specific example of an aqueous resin, an alkyd resin can be synthesized from a starting material similar to a conventional solvent-type alkyl resin, and the product can be obtained by subjecting a polybasic acid, a polyhydric alcohol, and an

oil component to a condensation reaction by an ordinary method. An acrylic resin can be obtained by copolymerizing an  $\alpha,\beta$ -ethylenic unsaturated acid (such as acrylic acid, methacrylic acid, or maleic acid), a (meth)acrylic acid ester (such as ethyl acrylate, propyl acrylate, butyl acrylate, methyl methacrylate, ethyl methacrylate, propyl methacrylate, or butyl methacrylate), and a vinyl aromatic compound (such as styrene or vinyl toluene). Examples of suitable epoxy resins include epoxy ester resins obtained by a method in which an epoxy ester is synthesized by reaction between an unsaturated fatty acid and the epoxy groups of an epoxy resin, and an  $\alpha,\beta$ -unsaturated acid is added to the unsaturated groups; a method for esterifying the hydroxyl groups of an epoxy ester and a polybasic acid such as phthalic acid or trimellitic acid; or the like.

Examples of suitable urethane resins include those obtained by the introduction of urethane groups into the resin backbone with the aid of a polyisocyanate compound (such as toluene diisocyanate, diphenylmethane diisocyanate, 1,6-hexane diisocyanate, or isophorone diisocyanate), and those obtained by the introduction of carboxyl groups with the aid of dimethylolpropionic acid.

When used after being rendered soluble in water, the aqueous resin is synthesized to an acid value of about 35–200, and the product is neutralized with an alkaline substance such as sodium hydroxide or amine, and is used for a water-based paint. When directly used as a dispersion type, the resin is set to a low acid value (about 5–35), and the product is neutralized and used for a water-dispersed paint.

Examples of suitable emulsions include emulsifier-dispersed emulsions obtained by a process in which an anionic or nonionic low-molecular surfactant is used to disperse an alkyd resin, acrylic resin, epoxy resin, or urethane resin; emulsion polymerization emulsions obtained by a process in which the aforementioned surfactants are used to emulsion-polymerize a (meth)acrylic acid ester, acrylonitrile, styrene, butadiene, vinyl acetate, vinyl chloride, or other monomer; and soap-free emulsions obtained by the emulsion polymerization and grafting of the aforementioned monomers with the aid of the following emulsion stabilizers:

maleinised polybutadiene, maleinised alkyd resin, maleinised fatty acid-modified vinyl resin, drying or semidrying fatty acid-modified acrylic resin, and other water-soluble resins.

It is particularly beneficial to add the aqueous pigment dispersion of the present invention to a water-based paint composed of low-acidity water-dispersed resins and emulsions with inferior pigment dispersibility. A particularly remarkable effect is obtained for low-acidity water-dispersed resins and emulsions that cure upon oxidation.

The ratio in which the aqueous pigment dispersion of the present invention is admixed into the water-based paint varies widely with the type of pigment in the dispersion, the degree of colouring required for the final paint, and the like. In common practice, the pigment dispersion is added in an amount of 2–1,000 weight parts per 100 weight parts of the resin content of the water-based paint.

The present invention will now be described in further detail through working examples. In the working examples, "parts" and "%" refer to parts by weight and percent by weight, respectively.

### Working Example 1

(1-a) The following components were introduced into a reactor:

Safflower oil fatty acids	236 parts
Glycidyl methacrylate	119 parts
Hydroquinone	0.4 part
Tetraethylammonium bromide	0.2 part

A reaction was allowed to occur under agitation at a temperature of 140–150°C, yielding an addition reaction product. The addition reaction between epoxy groups and carboxyl groups was traced while the amount of remaining carboxyl groups was measured. About 4 hours were needed to complete the reaction.

(1-b) *n*-Butyl cellosolve (350 parts) was introduced into a reactor and heated to 120°C. A mixture whose ratio is shown below was then added in drops to this solution over a period of about 2 hours. The reaction was performed under nitrogen injection.

Fatty acid-modified monomer obtained in (1-a) above	107 parts
Aron Macromonomer MM-5B (from Toagosei)	6 parts
<i>N</i> -vinylpyrrolidone	126 parts
Acrylic acid	11 parts
Azobisdimethyl valeronitrile	17.5 parts

The above mixture was added in drops while the reaction temperature was kept at 120°C and the reaction mixture was stirred. Azobisisobutyronitrile (2.5 parts) was added to the reaction solution 1 hour after the dropwise addition had been completed, another 2.5 parts of azobisisobutyronitrile was added to the reaction solution after two more hours, and the reaction was then performed for 2 hours while the temperature was kept at 120°C. The unreacted monomers and *n*-butyl cellosolve remaining after the reaction were distilled at a reduced pressure, yielding a copolymer solution with a heating residue of 70.2%, a resin acid value of 35.4, and Gardner viscosity K (40% *n*-butyl cellosolve solution). The copolymer was then neutralized

with triethylamine (1.0 equivalent neutralization), and water was added, yielding dispersant (I) composed of an aqueous solution with a heating residue of 40%.

A mixture of this dispersant (8.3 parts) and a titanium white pigment (R-5N from Sakai Chemical; 200 parts) was subsequently dispersed for 0.5 hour with the aid of a Red Devil disperser, yielding inventive aqueous pigment dispersion (A).

Inventive aqueous pigment dispersions (B) to (D) were obtained in the same manner from pigment dispersions whose compositions are shown in Table 1 below. Pigments other than titanium white were dispersed for 1 hour.

Table 1 below shows the properties of the resulting aqueous pigment dispersions.

The following components were then thoroughly mixed, yielding water-based paint (1): 10 parts of aqueous pigment dispersion (A) and 23.4 parts of a water-dispersed alkyd resin in the form of a 40% solution of solids obtained by neutralizing (1.0 equivalent) an alkyd resin that had an acid value of 16 and an oil length of 30 (starting material: linseed oil fatty acid/pentaerythritol/benzoic acid/isophthalic acid/maleic anhydride = 903/705/1140/610/45 (parts)).

The aqueous resins and pigment dispersions shown in Table 2 below were thoroughly mixed in the same manner, yielding water-based paints (2) to (6). Table 2 below shows the properties of films composed of the resulting water-based paints.

#### Working Example 2

(2-a) The following components were introduced into a reactor:

Safflower oil fatty acids	70.9 parts
Hydroquinone	0.03 part
<i>n</i> -Heptane	4.56 parts

The system was stirred and heated to 160°C. A mixture of the components shown below was subsequently added in drops to the 160°C reactor over a period of 2 hours.

Hydroxyethyl methacrylate	41.2 parts
Hydroquinone	0.03 part
Dodecylbenzenesulfonic acid	0.95 part
Toluene	3.7 parts

The resulting condensation water was removed from the reaction system, yielding a reaction product with an acid value of 5.5 and Gardner viscosity A<sub>2</sub>, whereupon the reactor pressure was lowered, and the toluene and *n*-heptane were removed at the reduced pressure, yielding a fatty acid-modified acrylic monomer with an acid value of 5.0 and Gardner viscosity A<sub>1</sub>.

(2-b) *n*-Butyl cellosolve (300 parts) was introduced into a reactor and heated to 120°C. A mixture whose composition is shown below was then added in drops to the solution over a period of about 2 hours. A reaction was conducted under nitrogen injection.

Fatty acid-modified monomer obtained in (2-a) above	35 parts
Aron Macromonomer MM-5M (from Toagosei)	30 parts
<i>n</i> -Butyl methacrylate	39 parts
<i>N</i> -vinylpyrrolidone	125 parts
Acrylic acid	11 parts
Azobisdimethyl valeronitrile	18 parts

The above mixture was added in drops while the reaction temperature was kept at 120°C and the reaction mixture was stirred. Azobisisobutyronitrile (2.5 parts) was added to the reaction solution 1 hour after the dropwise addition had been completed, another 2.5 parts of azobisisobutyronitrile was added to the reaction solution 2 hours after that, and the reaction was then performed for 2 hours while the temperature was kept at 120°C. The unreacted monomers and *n*-butyl cellosolve remaining after the reaction were distilled at a reduced pressure, yielding a copolymer solution with a heating residue of 70.0%, a resin acid value of 36.6, and Gardner viscosity L (40% *n*-butyl cellosolve solution). The copolymer was then neutralized

with triethylamine (1.0 equivalent neutralization), and water was added, yielding dispersant (II) composed of an aqueous solution with a heating residue of 40%.

The resulting dispersant (II) was subsequently used to disperse the pigment in Table 1 by the same method as in Working Example 1, yielding inventive aqueous pigment dispersion (E).

Pigment dispersion (E) and the aqueous resin shown in Table 2 below were thoroughly mixed together, yielding water-based paint (7).

Tables 1 and 2 below show the properties of pigment dispersion (E) and the performance of a film composed of water-based paint (7), respectively.

### Working Example 3

The following monomer mixture was polymerized by the method described in Working Example 1.

Fatty acid-modified monomer obtained in (1-a) above	40 parts
Aron Macromonomer MM-5M	45 parts
<i>N</i> -vinyl-2-pyrrolidone	150 parts
Acrylic acid	15 parts

The product was a copolymer solution with a heating residue of 70.4%, a resin acid value of 45.4, and Gardner viscosity K (40% *n*-butyl cellosolve solution). The solution was neutralized with triethylamine (1.0 equivalent neutralization), yielding dispersant (III) composed of an aqueous solution with a heating residue of 40%.

The resulting dispersant (III) was subsequently used to disperse the pigment in Table 1 by the same method as in Working Example 1, yielding inventive aqueous pigment dispersion (F).

Pigment dispersion (F) and the aqueous resin shown in Table 2 below were thoroughly mixed together, yielding water-based paint (8).

Tables 1 and 2 below show the properties of pigment dispersion (F) and the performance of a film composed of water-based paint (8), respectively.



#### Working Example 4

A polymerization reaction was performed under the same conditions as in Working Example 3 except that the same amount of *N*-vinyl carbazole was used instead of the *N*-vinyl-2-pyrrolidone employed in Working Example 3, yielding a copolymer solution with a heating residue of 71.2%, a resin acid value of 32.7, and Gardner viscosity M (40% *n*-butyl cellosolve solution). The solution was then neutralized with triethylamine (1.0 equivalent neutralization), yielding dispersant (IV) composed of an aqueous solution with a heating residue of 40%.

The resulting dispersant (IV) was subsequently used to disperse the pigment in Table 1 by the same method as in Working Example 1, yielding inventive aqueous pigment dispersion (G).

Pigment dispersion (G) and the aqueous resin shown in Table 2 below were thoroughly mixed together, yielding water-based paint (9).

Tables 1 and 2 below show the properties of pigment dispersion (G) and the performance of a film composed of water-based paint (9), respectively.

#### Working Example 5

A polymerization reaction was performed under the same conditions as in Working Example 1 except that 1-vinyl imidazole was used instead of the *N*-vinyl pyrrolidone employed in Working Example 1, yielding a copolymer solution with a heating residue of 70.8%, a resin acid value of 35.6, and Gardner viscosity N (40% *n*-butyl cellosolve solution). The solution was then neutralized with triethylamine (1.0 equivalent neutralization), yielding dispersant (V) composed of an aqueous solution with a heating residue of 40%.

The resulting dispersant (V) was subsequently used to disperse the pigment in Table 1 by the same method as in Working Example 1, yielding inventive aqueous pigment dispersion (H).

Pigment dispersion (H) and the aqueous resin shown in Table 2 below were thoroughly mixed together, yielding water-based paint (10).

Tables 1 and 2 below show the properties of pigment dispersion (H) and the performance of a film composed of water-based paint (10), respectively.

#### Comparative Example 1

Polymerization was done in the same manner as in Working Example 1 except that the same amount of *n*-butyl acrylate was used instead of the Aron Macromonomer MM-5B employed in Working Example 1, yielding a copolymer solution with a heating residue of 70.1%, a resin acid value of 35.2, and Gardner viscosity K (40% *n*-butyl cellosolve solution). The solution was then neutralized with triethylamine (1.0 equivalent neutralization), yielding dispersant (VI) composed of an aqueous solution with a heating residue of 40%.

The resulting dispersant (VI) was subsequently used to disperse the pigment in Table 1 by the same method as in Working Example 1, yielding aqueous pigment dispersion (I).

Pigment dispersion (I) and the aqueous resin shown in Table 2 below were thoroughly mixed together, yielding water-based paint (11). Tables 1 and 2 below show the properties of pigment dispersion (I) and the performance of a film composed of water-based paint (11), respectively.

Table 1

Working example		1						2	3	4	5	Comparative Example 1
Items	Pigment dispersion	(A)	(B)	(C)	(D)	(E)	(F)	(G)	(H)	(I)		
		(A)	(B)	(C)	(D)	(E)	(F)	(G)	(H)	(I)		
Dispersant	(I)	8.3	16.2	7.5	8.0							
	(II)					8.3						
	(III)						8.3					
	(IV)							8.3				
	(V)								8.3			
	(VI)										7.5	
Pigment <sup>*1</sup>	Titanium white R-5M	200				200	200	200	200			
	Carbon MA		60									
	Copper Phthalocyanine Blue			90							90	
	Mapico Yellow XLO				85							
Properties	Pigment/dispersant (solids weight ratio)	60/1	9/1	30/1	27/1	60/1	60/1	60/1	60/1		30/1	
	Pigment content (%)	74.8	27.5	52.2	54.8	75.0	74.9	74.8	74.7		52.2	
	Grain size <sup>*2</sup> (μ)	5	5	5	5	5	5	5	5		5	
	Viscosity (60 rpm), poise	23	30	3.1	20	23	21	23	15		14	
Storage stability (20°C, 1 week)	Condition	Good	Good	Good	Good	Good	Good	Good	Good		Hard caking	
	Viscosity (60 rpm), poise	23	26	2.9	21	22	20	22	14			

Table 2

Working examples		1						2	3	4	5	Comparative Example 1
Item	Water-based paint	(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)	(9)	(10)	(11)
Pigment dispersion	(A)	10	10	10								
	(B)				10							
	(C)					10						
	(D)						10					
	(E)							10				
	(F)								10			
	(G)									10		
	(H)										10	
	(I)											10
	Water-dispersed alkyd resin	23.4			137.5	65.3	13.7	18.8	23.4	23.4	23.4	
Aqueous resin	Emulsion <sup>*3</sup> (a)		23.4									
	Emulsion <sup>*4</sup> (b)			18.7								
Pigment/resin (solids weight ratio)		0.8/1.0	0.8/1.0	0.8/1.0	0.05/1.0	0.2/1	1.0/1.0	0.8/1.0	0.8/1.0	0.8/1.0	0.8/1.0	0.8/1.0
Paint film performance	Film thickness ( $\mu$ )	38	46	40	36	37	38	35	38	35	34	41
	Gloss(60°)	95	90	93	97	96	84	93	80	93	95	85
	Crosscut adhesion	Pass	Pass	Pass	Pass	Pass	Pass	Pass	Pass	Pass	Pass	Pass
	Water resistance	Good	Good	Good	Good	Good	Good	Good	Good	Good	Good	Good
	Pencil hardness	B	F	F	B	B	B	B	B	B	B	HB

- \*1 Titanium white R-5N: Titanium oxide from Sakai Chemical  
Carbon MA: Carbon black from Mitsubishi Chemical Industries  
Mapico Yellow XLO: Yellow pigment from Titan Kagaku
- \*2 Measured according to ASTM D1201-64
- \*3 Emulsion (solids: 40%) obtained by a process in which the water-dispersed alkyd resin used in Working Example 1 was neutralized to an acid value of 60 and used as an emulsion stabilizer in an amount of 30 parts to polymerize 70 parts of *n*-butyl acrylate
- \*4 Emulsion (solids: 50%) obtained by a process in which a dodecylbenzene sodium salt was used as an emulsion stabilizer to polymerize a monomer mixture comprising styrene/methyl methacrylate/*n*-butyl methacrylate (35/15/50)

[Merits of the Invention]

An aqueous dryer (Dicnate® from Dainippon Ink & Chemicals; cobalt metal content: 3%) was added to water-based paints (1) to (11) in an amount of 1 part per 100 parts of resin solids and applied to a soft steel plate. The coatings were tested after being dried for 3 days at a temperature of 20°C and a relative humidity of 75%.

Crosscut adhesion: 100 grid squares with a width of 1 mm were prepared, adhesive cellophane tape was affixed thereto, and tests were performed by peeling off the tape with considerable force.

Water resistance: Test pieces were immersed for 2 days in 20°C tap water, and the condition of the painted surface was visually examined.

Applicant: Kansai Paint Co., Ltd. (140)